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(54) Title: INSOLUBLE NANOFIBERS OF LINEAR POLY(ETHYLENIMINE) AND USES THEREFOR

(57) Abstract: An improved fiber for use in articles providing protection against chemical and nerve gas weapons is provided. Poly(ethylenimine) provides multiple amine sites for the nucleophilic decomposition of mustard gases and fluorophosphate nerve gases. Nanofibers of linear poly(ethylenimine) provide a lightweight protective fabric capable of capturing and neutralizing chemical warfare agents. Nanofibers provide a larger surface area per unit mass than traditional textile fabrics. Nanofibers of linear poly(ethylenimine) provide a greater surface area of material capable of the neutralization of chemical agents. A fabric comprising nanofibers of linear poly(ethylenimine) also provides for gas and water vapor permeability resulting in a more comfortable fabric. It also allows for use in protective breathing apparatuses.

INSOLUBLE NANOFIBERS OF LINEAR POLY(ETHYLENIMINE) AND USES THEREFOR

TECHNICAL FIELD

This invention relates generally to the production of fibers that can react chemically with nerve gases and other chemical warfare agents to render them inactive. More particularly, this invention relates to the production of insoluble fibers comprising crosslinked linear poly(ethylenimine) and ranging in diameter of from about 100 to about 1 micron, and more preferably, from about 100 nanometers to about 400 nanometers. The nanofibers are suitable for use in or on protective clothing and other fabrics and are insoluble in all solvents, including water, alcohol, and copper-containing water.

BACKGROUND OF THE INVENTION

Chemical warfare agents, including but not limited to sarin, soman, tabun, and mustard gas, have been used by combatants in warfare throughout this past century and continue to be a potential threat to combatants and non-combatants in future conflicts. Such agents have also be used against civilian populations in terrorist attacks. As a result, counter-measures against such agents are continually being sought for military and civilian uses. Protection must be afforded against not only inhalation of these agents, but in some cases, protection against absorption through the skin must also be given. Nerve gases such as Soman and VX are examples of nerve agents that can penetrate the skin.

Among the counter measures used to defend against such agents are breathing apparatuses and protective clothing. Clothing and fabrics containing charcoal absorbents or nonpenetrable plastic clothing have been developed and are now used for protection purposes. Unfortunately, this existing clothing is not water permeable and is, therefore, oftentimes uncomfortable to wear due to the fact that air and water vapor (e.g., perspiration) cannot pass through or penetrate the clothing. In addition, such clothing may also incorporate materials that bind chemical agents. These binding agents are typically used in such amounts that they contribute a relatively large amount of weight and bulk to the article of clothing. Existing breathing apparatuses suffer from

similar limitations.

Thus, a lightweight, breathable fabric, compatible with existing fabrics and permeable to both air and water vapor, but insoluble in all solvents and highly reactive with nerve gases and other deadly chemical agents, thereby rendering the gases or agents inactive, is believed highly desirable.

To that end, it is well known in the literature that primary amines catalyze decomposition of fluorophosphonates. Thus, attempts have been made to take advantage of this known characteristic of primary amines. For example, Wu U.S. Patent No. 5,391,426, the disclosure of which is incorporated herein by reference, teaches the use of a gas(and air)-blocking, water vapor-permeable polymeric coating comprising a crosslinked polyalkylenimine wherein the alkylene moiety has from 2 to 8 carbon atoms, on a pliable substrate that is also permeable to water vapor. The polyalkylenimine forms a coating or film on the surface of the substrate which is non-porous and air-impermeable. This polymeric coating, however, is shown to react with Soman and mustard gas and, therefore, can be said to prevent or reduce nerve gas penetration in to or through the substrates which are preferably, polymeric fabrics. While the coating set forth in the Wu patent is believed to have achieved an important advance in the fight against chemical warfare agents, it nevertheless still has its drawbacks. In particular, while the protective polymeric coating is water vapor permeable, it is not air permeable. Thus, fabrics produced by the process set forth in the Wu patent still were not suitable for uses other than clothing. For instance, the Wu patent offers essentially no advantage for breathing apparatuses, or fabrics and cloths where air must be allowed to permeate the fabric which contains the protective layer. The nonporous protective coating material of Wu is also not capable of being woven into the material of the fabric itself.

The technique of electrostatic spinning, also known within the fiber forming industry as electrospinning, of liquids and/or solutions capable of forming fibers, is well known and has been described in a number of patents as well as in the general literature. The process of electrostatic spinning generally involves the introduction of a liquid into an electric field, so that the liquid is caused to produce fibers. These fibers are generally drawn to a cathode for collection. During the drawing of the liquid, the fibers harden and dry. This may be caused by cooling of the liquid, i.e., where the liquid is normally a solid at room temperature; by evaporation of a solvent,

e.g., by dehydration (physically induced hardening); or by a curing mechanism (chemically induced hardening).

Fibers produced by this process have been used in a wide variety of applications, and are known, from U.S. Patent Nos. 4,043,331 and 4,878,908, to be particularly useful in forming non-woven mats suitable for use in wound dressings and prosthetic devices. One of the major advantages of using electrostatically spun fibers is that these fibers can be produced having very thin diameters, usually on the order of about 100 nanometers to about 25 microns, and more preferably, on the order of about 100 nanometers to about 4 microns. Thus, these fibers can be collected and formed into non-woven mats or membranes of any desired shape and thickness. It will be appreciated that, because of the very small diameter of the fibers, a mat or membrane with very small interstices and high surface area, two characteristics that are important in determining the porosity of the mat or membrane, can be produced.

Thus, the need exists for a poly(alkylenimine) electrospun nanofiber (i.e., a fiber having a diameter of less than about 1 micron) which is air and water vapor permeable, but is capable of chemically reacting with any nerve gas in the air to render it inactive. While various attempts have been made to employ such branched polyamines as a film or coating, there has not as of yet been a method for forming nanofibers of poly(ethylenimine) or the like suitable for use in fabrics in this purpose. The main reason for this is that linear poly(ethylenimine) (L-PEI) is known to be water insoluble, but soluble in alcohols and other organic solvents. In order to electrospin a fiber, it must first be in liquid form (i.e., soluble), but in order to render it effective against the chemical warfare agents and nerve gases, it must be insoluble. The resolution of this apparent, inherent conflict is achieved by the present invention.

SUMMARY OF INVENTION

It is, therefore, an object of the present invention to provide a fiber having a very large surface area per unit mass which fiber can detoxify chemical warfare agents and nerve gases by chemically modifying the nerve gas and rendering it inactive.

It is another object of the present invention to provide a fiber, as above, which has been electrostatically spun.

It is yet another object of the present invention to provide a fiber, as

above, produced from poly(ethylenimine).

It is still another object of the present invention to provide a fiber, as above, which, as an end result, will be insoluble in all solvents, including water, alcohols including ethanol, and copper-containing water.

It is a further object of the present invention to provide an improved protective covering wherein the covering is comprised of nanofibers of linear poly(ethylenimine).

It is yet a further object of the present invention to provide a plurality of fibers that can be made into a fabric, or can be placed in other fabrics or coverings as a breathable, lightweight protective shroud that can be quickly deployed as needed.

It is still a further object of the present invention to provide a protective fabric or covering, as above, which is permeable to air and water vapor.

It is yet a further object of the present invention to provide a protective fabric or covering, as above, which is compatible with existing fabrics.

At least one or more of the foregoing objects, together with the advantages thereof over the known art relating to electrostatic fiber spinning and the neutralization of chemical nerve agents, which shall become apparent from the specification that follows, are accomplished by the invention as hereinafter described and claimed.

In general, the present invention provides a fabric comprising a plurality of fibers of a linear poly(alkylenimine) which are insoluble in water, alcohol, or copper-containing water, and are capable of detoxifying chemical warfare agents and nerve gases, wherein the fabric is water vapor and gas permeable.

The present invention also provides a method of making a fabric capable of protecting against attack by chemical warfare agents and nerve gases, the method comprising electrospinning linear poly(ethylenimine) into a plurality of fibers and crosslinking the fibers to render the fibers insoluble.

This invention also provides a method of protecting a subject against attack by chemical warfare agents and nerve gases comprising covering the subject to be protected with a fabric comprising a plurality of fibers of a linear poly(alkylenimine) which are insoluble in water, alcohol, or copper-containing water, and are capable of detoxifying chemical warfare agents and nerve gases, wherein the fabric is water vapor

and gas permeable.

These and other aspects and objects of the present invention are achieved by a protective fabric comprising a plurality of crosslinked fibers of linear poly(ethylenimine). The fibers are preferably electrostatically spun to provide a thin diameter of less than about 4 microns (preferably, less than one micron) and, therefore, have a high surface area per unit mass far in excess of textile fibers. These fibers are also preferably insoluble in all solvents, including water, alcohol and copper-containing water. Most importantly however, these fibers provide multiple useful secondary amine sites for the nucleophilic decomposition of various chemical warfare agents such as mustard gases or fluorophosphate nerve gases such as sarin, soman, and tabum.

Other aspects and objects of the present invention are achieved by a protective covering comprising a plurality of crosslinked fibers of linear poly(ethylenimine) electrospun onto a support fabric containing textile fibers. Where the electrospun fibers are blended into the support fabrics, it will be appreciated that, even if the blended covering contains only a few percent by weight of the nanofibers of the present invention, most of the surface area in the fabric will still be that of the nanofibers given the extreme differential in surface areas between textile fibers and electrospun fibers. Thus, this blended fabric will also have the ability to capture and neutralize the chemical warfare agents and nerve gases, with only minimal effects on the ordinary useful properties of the support fabric.

EMBODIMENTS FOR CARRYING OUT THE INVENTION

As noted hereinabove, the present invention is directed toward the production and use of electrospun fibers of linear poly(ethylenimine) having diameters of less than about 1 micron, more preferably, less than about 500 nanometers, and most preferably, from about 100 to about 400 nanometers. Such fibers, when spun to form nanoporous membranes by themselves, or when spun on supporting fabrics, provide multiple secondary amine sites for nucleophilic decomposition of mustard gases and fluorophosphate nerve gases such as sarin, soman, and tabum. Because the fibers are produced by electrospinning techniques, the surface area per unit mass of the fibers is much higher than is the surface area for even the smallest commonly known textile fibers. Moreover, the fabrics or membranes formed from the fibers are at least

somewhat porous, typically having interstices on the micron or nanometer scale. This allows for the fabrics or membranes to be breathable to both air and water vapor, while maintaining its highly efficient defense against those nerve gases which are based on highly electrophilic or nucleophilic centers of reactivity.

In order to demonstrate practice of the present invention, linear poly(ethylenimine) must first be prepared. While any linear poly(alkyleneimine) wherein the alkylene moiety has 2 to 8 carbon atoms could be employed, the preferred embodiment employs poly(ethylenimine). Linear poly(ethylenimine) may be prepared by any method known in the art or may be obtained commercially, if available. One well known and published method of synthesizing linear poly(ethylenimine) is by hydrolysis of poly(2-ethyl-2-oxazoline). This method is well known to those skilled in the art and, therefore, details of the process are not provided herein. Typically, the poly(2-ethyl-2-oxazoline) should have a number average molecular weight of about 500,000, although small or larger molecular weights should not readily affect the formation of linear poly(ethylenimine). In a preferred embodiment, the linear poly(ethylenimine) synthesized should have a molecular weight ranging from about 100,000 to about 500,000, although higher or lower molecular weights are not seen as materially affecting the essential nature of the invention, provided of course, the compound can be effectively dissolved in the desired solvent for use in electrospinning fibers therefrom.

Linear poly(ethylenimine) (L-PEI) is known to be water insoluble, but soluble in alcohols or other organic solvents. Consequently, linear poly(ethylenimine) can be dissolved in essentially any solvent known in the art in which it is known to be dissolvable, with a concentrated alcohol solution being preferred. The concentration of the alcohol solution is, again, not materially important to the success of the invention, provided of course that the solution is capable of dissolving of linear poly(ethylenimine). Typically, about 10 percent by weight of linear poly(ethylenimine) may be dissolved in the solution, although higher or lower amounts can be used without departing from the scope or spirit of the invention.

Once the linear poly(ethylenimine) is dissolved, the concentrated alcohol solutions of linear poly(ethylenimine) can be used with known electrospinning techniques to electrospin and form fibers of linear poly(ethylenimine). These fibers

typically have a diameter of from about 100 nanometers to about 1 micron, and more preferably, in the range of from about 100 nanometers to about 400 nanometers. In light of the diameter size of the fibers, these fibers are often termed "nanofibers."

It will be appreciated that the resultant nanofibers have very high surface areas per unit mass. Thus, when these fibers are used to form a mat or a membrane, the resultant mat, while porous, will have very small intertices and high surface areas.

It will further be appreciated that the fibers, when spun into a mat or membrane are not soluble in water, but remain soluble in alcohol and in copper containing water solutions. However, suitable fabrics for use in fighting chemical warfare agents should be insoluble in all solvents. Therefore, in order to render these fibers insoluble in all solvents, it is necessary to crosslink the linear poly(ethylenimine) fibers.

Crosslinking of the fibers can be accomplished by any manner known in the art. One preferred method is to soak the fibers in minimum (less than 25 percent by weight, and more preferably, less than about 1 percent by weight) amounts of 1,4-butanediol diglycidyl ether (i.e., bis-epoxide) in ethanol and then to cure the fibers for about five minutes at about 80°C. The resultant crosslinked linear poly(ethylenimine) nanofibers are then rendered insoluble in all solvents including ethanol, water, and copper containing water solutions.

Alternatively, the solution of linear poly(ethylenimine) could be crosslinked prior to being electrospun into fibers. For example, linear poly(ethylenimine), either in solution or by itself, could be mixed with from about 1 to about 25 percent by weight bis-epoxide in ethanol and then electrospun into the desired fibers. Where this process is employed, the crosslinking agent, i.e., the bis-epoxide, would then be resident within the fiber and, upon curing of the fibers at about 80°C for about 1 to about 30 minutes, the fiber would become crosslinked.

Once the fibers are produced, they can be used in any of a number of applications. Because the fibers will have numerous secondary amine sites available for the nucleophilic decomposition of the various gases above described, the fibers are particularly suited for use as highly effective protective fabrics or coverings against known chemical warfare agents or nerve gases. Furthermore, the fibers of the present invention are compatible with other textile fabrics and may be used therewith.

Consequently, protective clothing and breathing apparatus using such protective coverings or fabrics may be thereby rendered breathable to air and water vapor and lightweight.

It should thus be evident that the present invention is highly effective in providing insoluble nanometer-sized (in diameter) fibers of linear poly(ethylenimine) suitable for use as a protective covering or shroud capable of detoxifying nerve gases and other chemical warfare agents. The fibers, either by themselves or with additional support fabrics, can be used to provide lightweight, highly efficient protective clothing or other fabrics which are permeable to both air and water vapor.

Where the electrospun fibers are blended into support fabrics, it will be appreciated that, even if the blended covering contains only a few percent by weight of the nanofibers of the present invention, most of the surface area in the fabric will still be that of the nanofibers given the extreme differential in surface areas between textile fibers and electrospun fibers. Thus, this blended fabric will also have the ability to capture and neutralize the chemical warfare agents and nerve gases, with only minimal effects on the ordinary useful properties of the support fabric. The use of the nanofibers of the present invention allows for air to permeate the resultant covering as well. Thus, the fibers of the present invention may also be suitable for use in a protective breathing apparatus. It is also envisioned that the fibers of the present invention may be used in a shroud to cover one or more individuals in the event of a chemical agent or nerve gas attack. Such an embodiment may be particularly useful in response to an unanticipated attack on civilians.

Based upon the foregoing disclosure, it should now be apparent that the use of nanofibers of linear poly(ethylenimine) will carry out at least one of the objects set forth hereinabove. It is, therefore, to be understood that any variations evident fall within the scope of the claimed invention and thus, the selection of specific component elements can be determined without departing from the spirit of the invention herein disclosed and described.

CLAIMS

We claim:

1. A fabric comprising:

a plurality of fibers of a linear poly(alkylenimine) which are insoluble in water, alcohol, or copper-containing water, and are capable of detoxifying chemical warfare agents and nerve gases, wherein the fabric is water vapor and gas permeable.

2. The fabric of claim 1, wherein the fibers provide multiple useful secondary amine sites for the nucleophilic decomposition of various chemical warfare agents such as mustard gases or fluorophosphate nerve gases such as sarin, soman, and tabum.

3. The fabric of claim 1, wherein the plurality of fibers form a woven fabric.

4. The fabric of claim 1, wherein the plurality of fibers form a non-woven fabric.

5. The fabric of claim 1, wherein the fibers are electrospun.

6. The fabric of claim 5, wherein the electrospun fibers each have a surface area per unit mass greater than the smallest fiber produced by textile means.

7. The fabric of claim 6, wherein the electrospun fibers have a diameter of less than 4 microns.

8. The fabric of claim 7, wherein the electrospun fibers have a diameter of less than 1 micron.

9. The fabric of claim 8, wherein the electrospun fibers have a diameter of from about 100 to about 400 nanometers.

10. The fabric of claim 1, wherein the linear poly(alkylenimine) contains 2 to 8 carbon atoms.

11. The fabric of claim 10, wherein the linear poly(alkylenimine) is linear poly(ethylenimine).

12. The fabric of claim 1, further comprising at least one support fabric not containing fibers of linear poly(alkylenimine) wherein the fibers of linear poly(alkylenimine) are blended into said support fabric.

13. An item of protective clothing comprising the fabric of claim 1.

14. A breathing apparatus comprising the fabric of claim 1.

15. A method of making a fabric or membrane capable of protecting against attack by chemical warfare agents and nerve gases, the method comprising:

electrospinning linear poly(ethylenimine) into a plurality of fibers; and

crosslinking the fibers to render the fibers insoluble.

16. The method of claim 15, wherein the step of electrospinning includes solubilizing linear poly(ethylenimine) in a solvent and electrospinning the solution of linear poly(ethylenimine) into the fibers.

17. The method of claim 16, wherein the solvent is an alcohol.

18. The method of claim15, wherein the fibers each have a surface area per unit mass greater than the smallest fiber produced by textile means.

19. The method of claim 18, wherein the electrospun fibers have a diameter of less than 4 microns.

20. The method of claim 19, wherein the electrospun fibers have a diameter of less than 1 micron.

21. The method of claim 15, wherein the linear poly(ethylenimine) has an average molecular weight of between about 100,000 and about 500,000.

22. The method of claim 15, wherein the fibers provide multiple useful secondary amine sites for the nucleophilic decomposition of various chemical warfare agents such as mustard gases or fluorophosphate nerve gases such as sarin, soman, and tabum.

23. A method of protecting a subject against attack by chemical warfare agents and nerve gases, comprising:

covering the subject to be protected with a fabric comprising a plurality of fibers of a linear poly(alkylenimine) which are insoluble in water, alcohol, or copper-containing water, and are capable of detoxifying chemical warfare agents and nerve gases, wherein the fabric is water vapor and gas permeable.

24. The method of claim 23, wherein the nanofibers have a diameter of about 100 to about 400 nanometers.

25. The method of claim 23, wherein the fabric additionally comprises supporting textile fibers.

26. The method of claim 23, wherein the article is selected from the group consisting of an article of protective clothing, a protective breathing apparatus, and a protective shroud.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :D03D 15/00; D04H 1/00
US CL :57/402; 442/181, 239, 268, 327, 351
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 57/402; 442/181, 239, 268, 327, 351

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,043,331 A (MARTIN et al) 23 August 1977, see entire document.	1-26
A	US 3,976,604 A (ROBERTS et al) 24 August 1976, see entire document.	1-26
A	US 3,644,251 A (WILHELMI) 22 February 1972, see entire document.	1-26

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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